# Supporting Information

## Pascal et al. 10.1073/pnas.1108073108

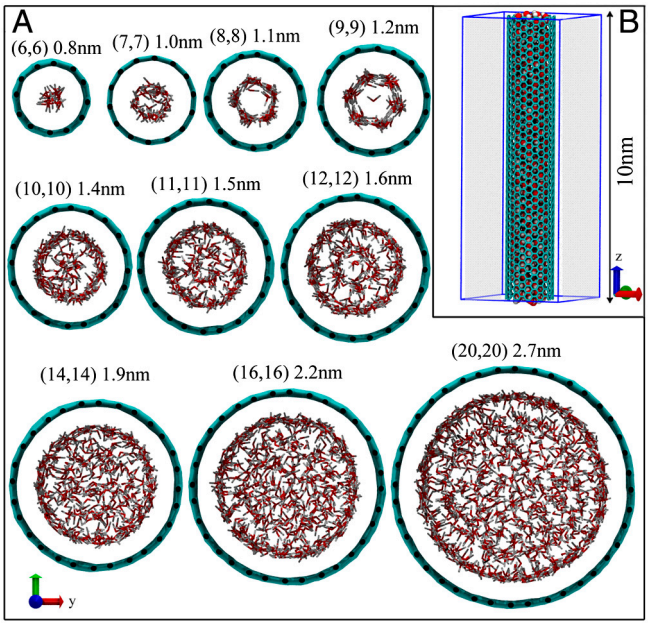


**Fig. S1.** (*A*) Equilibrium molecular dynamics (MD) structure of the 10 nanotubes considered in this study. Each structure is the last snapshot of a 5-ns constant temperature and constant pressure MD run with a finite nanotube. Water molecules outside the nanotube are not shown for clarity. (*B*) Schematic of the starting MD system configuration for infinite nanotube simulations. The equilibrium structures in *A* are inserted into a box of 14,000 preequilibrated simple point charge-extended waters (shown in gray dots). All nanotubes are 10-nm long.

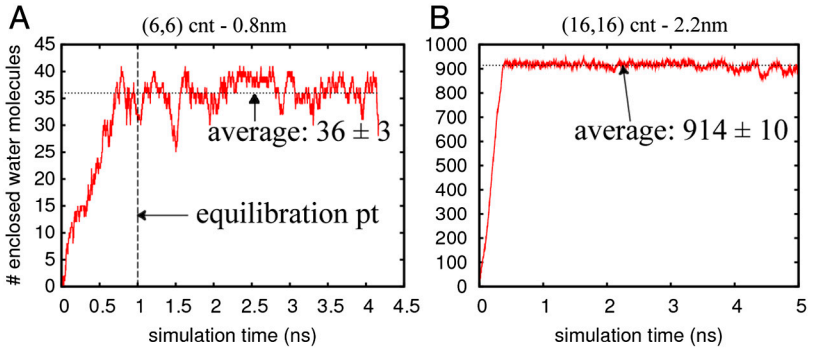


**Fig. S2.** Number of enclosed water molecules in finite open-ended carbon nanotube (CNT); (*A*) 0.8-nm (6,6) CNT; (*B*) 2.2-nm (16,16) CNT over 5 ns of constant temperature and constant pressure (NPT) dynamics. Convergence is seen after 1 ns of dynamics. The snapshot with number of enclosed waters closest to the average during the last 4 ns (Table S1) was used to form an infinite nanotube and solvated with simple point charge-extended waters (10 Å buffer in the *x* and *y* dimension) for long-term NPT dynamics.

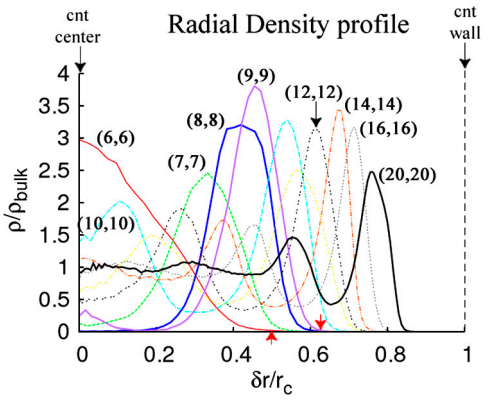


**Fig. S3.** Radial density profile (RDensF) of water molecules inside the 10 carbon nanotubes (CNTs) in this study normalized by the bulk density (0.97 g/mL). The number of water molecules in a cylindrical volume element $\delta r = 0.1$ Å from the CNT center ($\delta r/r = 0$) to the CNT walls ($\delta r/r = 1$) is determined every 10 ps of the last 25-ns constant temperature and constant pressure dynamics. The RDensFs for the (6,6) (solid red), (8,8) (solid blue), and (9,9) (solid purple) are emphasized. In the case of the (6,6) (single-file water), the water molecules are primarily in the center of the tube, but are mobile with significant lateral diffusion. The (8,8) and (9,9) CNTs form rigid pentagonal and hexagonal motifs nearer the CNT walls and have little density at the CNT center. The (12,12) (dashed black), (14,14) (dashed orange), (16,16) (dotted black), and (20,20) (solid black) CNTs all have density profiles similar to bulk water. When calculating the effective density $\rho_{\text{eff}}$ (Table S2), we integrate the RDensF over the radius region defined by the CNT center and the end of the profile, as exemplified for the cases of (6,6) (upward red arrows) and the (8,8) and (9,9) (downward red arrows) CNTs.

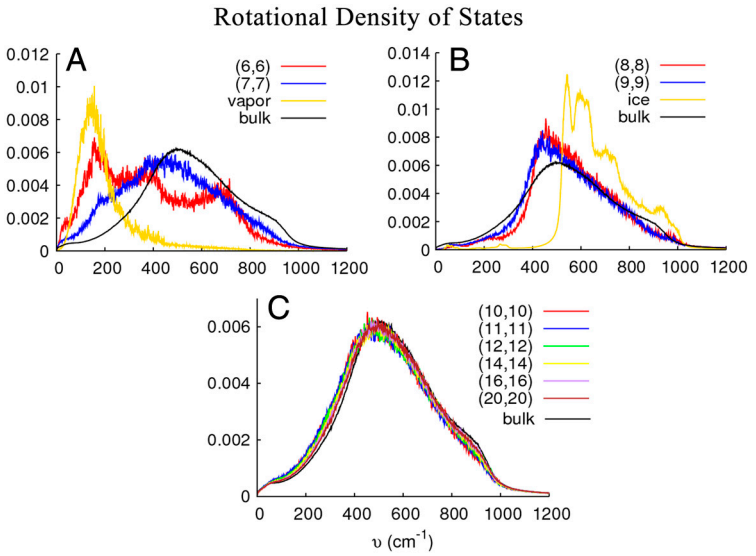


**Fig. S4.** Rotational densities of state spectrum normalized by number of molecules in the system. (*A*) Comparison of waters confined inside (6,6) (red) and (7,7) (blue) carbon nanotubes (CNTs) compared to water vapor (yellow) and bulk water (black). The water vapor was simulated at a density of 0.0007 g/mL at 350 K and 1 atm with statistics collected from the last 5 ns of a 20-ns simulation. (*B*) Comparison of the waters confined inside the (8,8) (red) and (9,9) (blue) CNTs compared to ice (yellow) and bulk water (black). The ice was simulated at a density of 0.92 g/mL at 150 K and 1 atm with statistics collected from the last 5 ns of a 20-ns simulation. (*C*) Comparison of waters confined inside the (10,10) red, (11,11) blue, (12,12) green, (14,14) yellow, (16,16) purple, and (20,20) brown CNTs compared to the bulk. The rotational spectrums of waters in these CNTs are virtually indistinguishable from the bulk leading to similar rotational entropy.

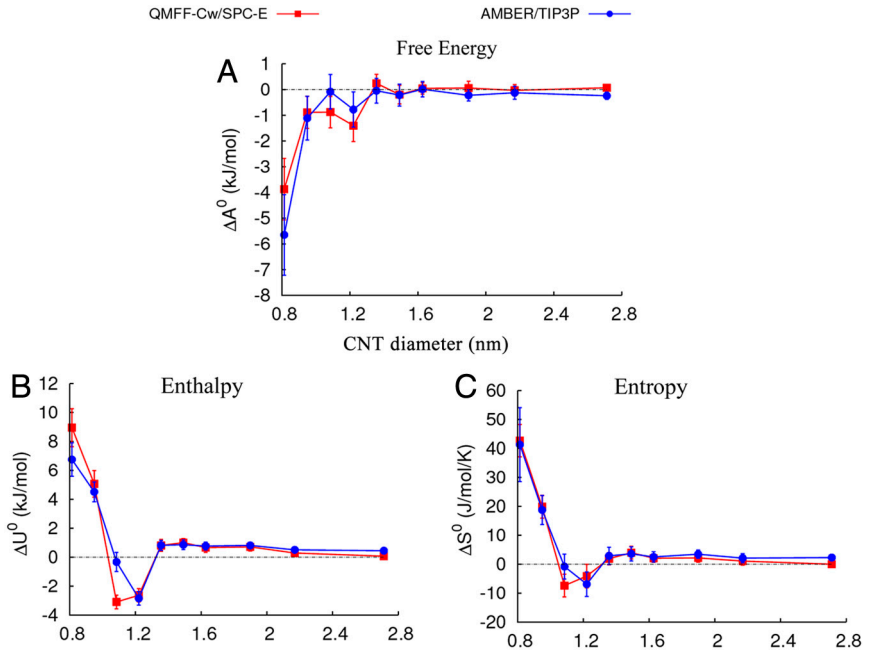


**Fig. S5.** Comparison of the (*A*) free energy $\Delta A^0$, (*B*) enthalpy $\Delta U^0$, and (*C*) entropy $\Delta S^0$ of water confined in 10 carbon nanotubes (CNTs) with the simple point charge-extended (SPC-E) water model (this study, red squares) and with the unoptimized parameters of the AMBER96 force field for carbon and the TIP3P water model (oxygen–carbon parameters of $\varepsilon_{C-O} = 0.392$ kJ/mol and $\sigma_{C-O} = 3.275$ Å, blue filled circles) (1). The good agreement indicates that the results presented in this study are fairly insensitive to the choice of interaction potentials. As a figure of merit, we calculate the free energy of water inside the 0.8-nm (6,6) CNT to be −3.98 kJ/mol using the two-phase thermodynamics method, which is in good agreement with the value of −3.34 kJ/mol in ref. 1 from potential of mean force calculations.

1 Hummer G, Rasaiah JC, Noworyta JP (2001) Water conduction through the hydrophobic channel of a carbon nanotube. *Nature* 414:188–190.

**Table S1. Description and results of finite molecular dynamics (MD) simulations**

| CNT | Initial unit cell dimensions, Å | | No. water molecules in unit cell | No. enclosed waters | |
|---|---|---|---|---|---|
| | *x*/*y* | *z* | | avg | ± |
| 6,6 | 28.14 | 127.17 | 9,393 | 36 | 2 |
| 7,7 | 29.50 | 127.17 | 12,949 | 102 | 2 |
| 8,8 | 30.85 | 127.17 | 14,618 | 172 | 3 |
| 9,9 | 32.20 | 127.17 | 16,253 | 219 | 4 |
| 10,10 | 33.56 | 127.17 | 17,923 | 294 | 6 |
| 11,11 | 34.92 | 127.17 | 19,624 | 369 | 5 |
| 12,12 | 36.28 | 127.17 | 21,174 | 465 | 5 |
| 14,14 | 39.00 | 127.17 | 24,499 | 673 | 6 |
| 16,16 | 41.70 | 127.17 | 27,978 | 913 | 7 |
| 20,20 | 47.13 | 127.17 | 34,969 | 1,536 | 7 |

Results are obtained from the last 4 ns of a 5-ns constant temperature and constant pressure run. The number of enclosed waters was obtained by counting all water molecules within a cylindrical region defined by the carbon nanotube (CNT) end caps and the CNT radius.

**Table S2. Density of water molecules inside carbon nanotubes (CNTs) during the last 4 ns of 5-ns constant temperature and constant pressure dynamics**

| CNT | CNT diameter, nm | | Total density, g/mL | | Effective density, g/mL | |
|---|---|---|---|---|---|---|
| | avg | ± | avg | ± | avg | ± |
| 6,6 | 0.8256 | 0.0008 | 0.202 | 0.013 | 0.496 | 0.048 |
| 7,7 | 0.9612 | 0.0006 | 0.425 | 0.010 | 0.887 | 0.039 |
| 8,8 | 1.0954 | 0.0006 | 0.552 | 0.004 | 1.034 | 0.027 |
| 9,9 | 1.2300 | 0.0006 | 0.562 | 0.006 | 0.963 | 0.014 |
| 10,10 | 1.3664 | 0.0008 | 0.605 | 0.012 | 0.983 | 0.018 |
| 11,11 | 1.5020 | 0.0008 | 0.627 | 0.008 | 0.972 | 0.020 |
| 12,12 | 1.6368 | 0.0366 | 0.667 | 0.007 | 0.990 | 0.011 |
| 14,14 | 1.9094 | 0.0008 | 0.708 | 0.006 | 0.989 | 0.012 |
| 16,16 | 2.1802 | 0.0010 | 0.738 | 0.006 | 0.983 | 0.011 |
| 20,20 | 2.7248 | 0.0010 | 0.795 | 0.004 | 0.994 | 0.007 |

The total density assumes an internal volume defined by the entire CNT diameter. The effective density has an effective radius which accounts for the carbon van der Waals radii. Convergence to the bulk density begins to be seen approximately after the (10,10) CNT.